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Spin Maximization: Switching of the Usual $S = 11$ State of $Mn^{II}_4Mn^{III}_3$ Disklike Complexes to the Maximum $S = 16$

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The $S = 11$ ground states of the Mn_7 family of mixed-valence complexes with a metal-centered hexagonal topology have been found by density functional theory calculations to arise by spin frustration involving small differences in the magnitudes of the two weakest interactions controlling the alignment of the central spin. Targeted structural perturbation has allowed a complex with the central spin flipped to be discovered, which thus possesses the maximum $S = 16$ ground state.

Molecular materials possessing large numbers of unpaired electrons (i.e., a large ground-state spin, S) are a fascinating and important field spanning chemistry, physics, materials science, and medicine. At one extreme is the purely fundamental desire to understand exactly how the sign and relative magnitudes of the constituent exchange interactions yield the high S value. At the other are, for example, applications such as MRI imaging and a molecular route to nanoscale magnets (single-molecule magnets).[1] For such reasons, we have recently developed a general interest in understanding and attaining some rudimentary level of control of S in such often high-nuclearity molecules.[2]

Large S values can arise from ferromagnetic interactions and/or competing antiferromagnetic interactions (spin frustration) in certain M_x topologies that prevent (frustrate) the preferred antiparallel spin alignments.[3] Such spin-frustration effects are almost always present in high-nuclearity metal clusters containing multiple triangular M_3 subunits, and this complexity typically prevents a ready rationalization of the S value. Such an example is the family of Mn_7 clusters with a metal-centered hexagonal topology of six fused M_3 units; the mixed-valent ($4Mn^{II}$, $3Mn^{III}$) members have $S = 11$ ground states.[4] We have now discovered another $S = 11$ member of this family and decided it was time to determine computationally exactly how this ground state results.

The reaction of $Mn(ClO_4)_2 \cdot 6H_2O$, *N*-methyldiethanolamine ($mdaH_2$), NaN_3, and NEt_3 in a 1:2:1:2 molar ratio in *N,N*-dimethylformamide (DMF)/MeOH gave a dark-red solution that upon layering with Et_2O gave dark-red crystals of $\{[Na(MeOH)_3][Mn_7(N_3)_6(mda)_6]\}_n$ (**1**) in 55% yield.[5] The anion of **1** (Figure 1) has virtual C_3 symmetry and consists of a near-planar Mn_7 unit comprising a central Mn atom held within a Mn_6 hexagon by six μ_3-RO^- alkoxide arms of six mda^{2-} groups. The remaining mda^{2-}-RO^- arms bridge Mn_2 pairs of the hexagon, and the N atoms are terminally bound, as are the six N_3^- groups. Charge considerations and bond-valence-sum (BVS) calculations[6] confirm a trapped-valence $4Mn^{II}$, $3Mn^{III}$ description, which is further supported by clear Jahn−Teller axial elongations at the near-octahedral Mn^{III} atoms. The $[Na(MeOH)_3]^+$ cation forms two $Na-N_3^-$ contacts ($\sim$2.4 Å) between adjacent anions, making the Na^+ five-coordinate.

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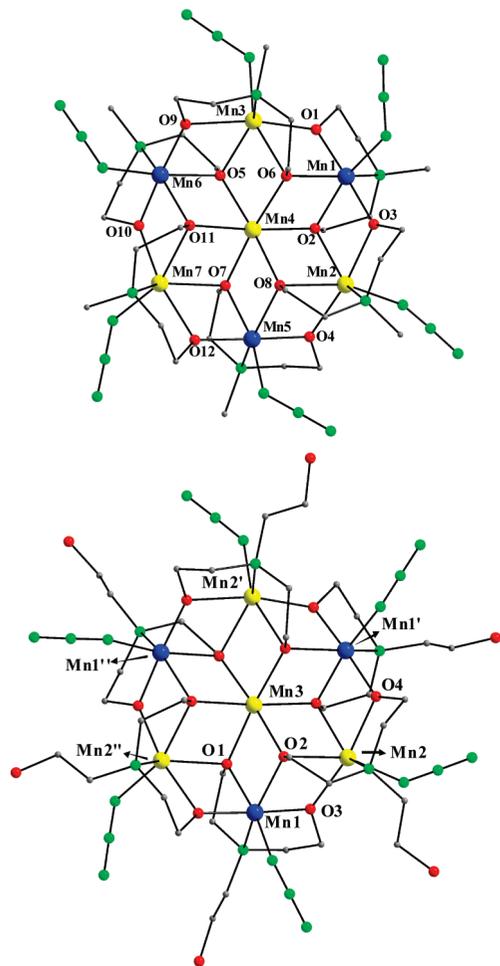
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(5) Anal. Calcd (found) for dried **1** (solvent-free): C, 27.17 (27.12); H, 5.39 (5.52); N, 23.05 (23.14). Anal. Calcd (found) for **2**·DMF: C, 28.99 (28.82); H, 5.30 (5.19); N, 21.67 (21.68). Crystal data for **1**·MeOH: $C_{34}H_{82}N_{24}O_{16}Mn_7Na$, 1490.81 g mol^{-1}, monoclinic *Cc*, *a* = 17.2034(8) Å, *b* = 15.4286(7) Å, *c* = 22.9340(11) Å, β = 98.398(1)°, *Z* = 4, *V* = 6022.0(5) Å^3, d_{calcd} = 1.644 g cm^{-3}, *T* = 173(2) K. Final R1 = 4.29 and wR2 = 9.90. Crystal data for **2**·DMF·Et_2O: $C_{41}H_{95}N_{25}O_{20}Mn_7Na$, 1665.99 g mol^{-1}, rhombohedral *R*3, *a* = 15.8536(6) Å, *b* = 15.8536(6) Å, *c* = 22.7938(12) Å, *Z* = 3, *V* = 4961.4(4) Å^3, d_{calcd} = 1.673 g cm^{-3}, *T* = 173(2) K. Final R1 = 3.48 and wR2 = 9.06.

Figure 1. Molecular structures of the anions of **1** (top) and **2** (bottom). H atoms have been omitted for clarity. Color scheme: Mn^{II}, yellow; Mn^{III}, blue; O, red; N, green; C, gray.
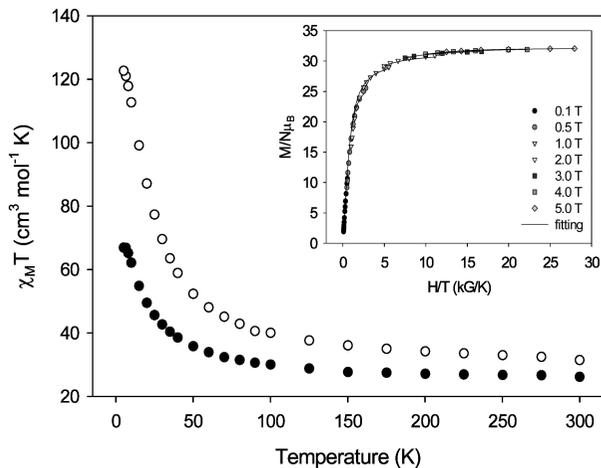

Figure 2. $\chi_M T$ vs T plots for complexes **1** (●) and **2·**DMF (○) in a 1 kG field. Inset: Plot of $M/N\mu_B$ vs H/T for **2·**DMF at the indicated fields. The solid lines are the fit of the data; see the text for the fit parameters.

Solid-state direct current magnetic susceptibility (χ_M) data on dried **1** were collected in a 1 kG (0.1 T) field in the 5.0−300 K range and are plotted as $\chi_M T$ vs T in Figure 2. $\chi_M T$ steadily increases from 26.15 cm^3 K mol^{-1} at 300 K to a maximum of 65.81 cm^3 K mol^{-1} at 6.5 K and then decreases to 65.78 cm^3 K mol^{-1} at 5.0 K; the latter is assigned to Zeeman effects, zero-field splitting, and weak
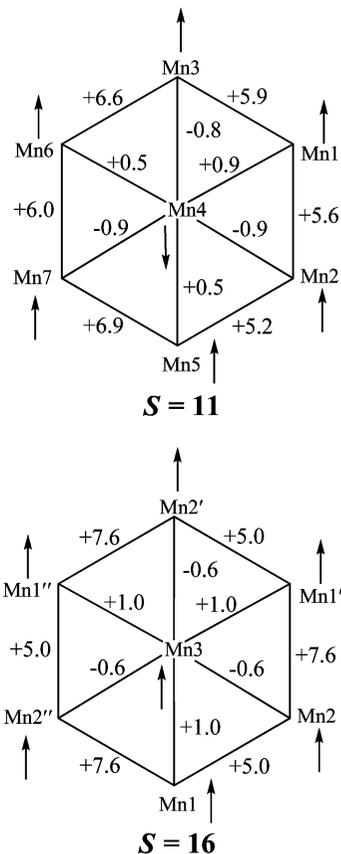
Figure 3. Calculated J values obtained by DFT of the anions of **1** (top) and **2** (bottom), using the $\mathscr{H} = -2J_{ij}\hat{S}_i\cdot\hat{S}_j$ convention, and the resulting ground-state spin alignments. The atom labels are those of Figure 1.

intermolecular interactions mediated by the interanion Na$^+$ contacts. The data indicate an $S = 11$ ground state and $g < 2$, as expected for Mn. $S = 11$ was confirmed by fitting of magnetization (M) data collected in the 0.1−5 T and 1.8−10.0 K ranges by matrix diagonalization and including axial zero-field splitting ($D\hat{S}_z^2$), the Zeeman interaction, and a full powder average, which gave $S = 11$, $g = 1.95$, and $D = -0.15$ cm^{-1}.[7]

Complex **1** is thus yet another $S = 11$ member of this disklike Mn$_7$ (4Mn^{II}, 3Mn^{III}) family.[4] To gain an understanding of exactly how this ground state originates, we have carried out density functional theory (DFT) calculations on the complete anion using the crystallographic coordinates.[8] The calculated Mn$_2$ exchange parameters J_{ij} are summarized in Figure 3 (top) and clearly explain the $S = 11$ state on the basis of spin frustration. The outer J(Mn^{2+},Mn^{3+}) interactions ($J_{23(o)}$) are all ferromagnetic and significantly stronger than the inner J(Mn^{2+},Mn^{2+}) ($J_{22(i)}$) and J(Mn^{2+},Mn^{3+}) ($J_{23(i)}$) interactions, aligning all outer spins parallel. The alignment of the central Mn^{2+} spin is thus determined by the different signs and relative magnitudes of $J_{22(i)}$ and $J_{23(i)}$; the former is the stronger, frustrating the latter and aligning the spin antiparallel to the outer hexagon, giving an $S = 11$ ground state. The spin alignments of Figure 3 (top) are confirmed

(6) Liu, W.; Thorp, H. H. *Inorg. Chem.* **1993**, *32*, 4102. BVSs for Mn^{2+}, Mn^{3+}, and Na$^+$ were 1.85−2.01, 2.89−2.91, and 1.12−1.25, respectively.
(7) See the Supporting Information.
(8) B3LYP functional with double-ζ DZVP basis set.

by the calculated spin couplings $\langle \hat{S}_i \cdot \hat{S}_j \rangle$,[7] showing, in particular, that the values of the latter for the Mn4Mn1, Mn4Mn5, and Mn4Mn6 pairs are negative even though these exchange interactions ($J_{23(i)}$) are all positive (ferromagnetic). In other words, these ferromagnetic interactions are completely frustrated, and the spins are aligned antiparallel.

The origin of the $S = 11$ ground state is thus simpler than we had anticipated: a strongly coupled $S = {}^{27}/_2$ outer hexagon and the overall molecular S determined by one factor, the relative magnitude of the weaker $J_{22(i)}$ and $J_{23(i)}$ interactions.[9] It now appeared likely that minor structural perturbations to the core could change the $J_{22(i)}$ vs $J_{23(i)}$ difference enough to flip the central spin and give the maximum $S = 16$ for this $4Mn^{II}$, $3Mn^{III}$ complex. We have thus been seeking this by small modifications to the ligation, seeking merely small structural perturbations, and thereby avoiding changes to the topology. New members of the family have been discovered, such as **1** with terminal Cl^- instead of N_3^-, but these were found to also possess $S = 11$ ground states.[10] Finally, however, we identified the desired $S = 16$ variant.

The same preparative procedure as that of **1** but employing triethanolamine (teaH$_3$) instead of mdaH$_2$ gave $\{Na[Mn_7(N_3)_6(teaH)_6]\}_n$ (**2**) in 63% yield. The anion has crystallographic C_3 symmetry and is essentially isostructural with that of **1** except for the mda^{2-} vs teaH^{2-} difference (Figure 1, bottom), with the third alcohol arm of the latter being protonated and bound to a Na^+ ion rather than Mn. $\chi_M T$ for **2**·DMF increases from 31.45 cm^3 K mol^{-1} at 300 K to 122.63 cm^3 K mol^{-1} at 5.0 K (Figure 2), indicating a much larger ground state S than that for **1**. Fitting of magnetization data gave $S = 16$, $g = 1.95$, and $D = -0.02$ cm^{-1} (Figure 2, inset). The $S = 11$ vs $S = 16$ difference for **1** vs **2** was further supported experimentally by in-phase alternating current (ac) susceptibility data in the $1.8-15$ K range using a 3.5 G ac field oscillating at $5-1500$ Hz.[10]

With **2**·DMF confirmed as $S = 16$, the origin of the latter was investigated by DFT, and the results are summarized in Figure 3 (bottom). The main and crucial difference is that the relative magnitudes of $J_{22(i)}$ and $J_{23(i)}$ have reversed; the ferromagnetic $J_{23(i)}$ is now stronger, aligning the central spin parallel to the outer hexagon and giving an $S = 16$ ground state. Small structural changes from the different ligand sets,

different packing arrangements, and forces, etc., have clearly caused the switch in the ground state by small changes to $J_{22(i)}$ and $J_{23(i)}$.[9,10]

In conclusion, we have shown that it is possible to alter $S = 11$ of the long-known Mn$_7$ family to its maximum $S = 16$, stimulated by the realization that the ground state is sensitive to the relative magnitude of the two *weakest* interactions, which should be the most susceptible to structural perturbation. This is a crucial point: before **1** and the DFT study, we had assumed the various J values to be of comparable magnitude, with $S = 11$ therefore resulting from a very complicated balance of several competing interactions and many intermediate-spin alignments. However, such a situation should make the ground state very sensitive to small changes in their relative magnitude, leading to a variety of ground states being observed,[2] inconsistent with the repeated occurrence of $S = 11$. In fact, the outer hexagon is (relatively) strongly coupled ferromagnetically, and this observation was both the rationalization of the recurring $S = 11$ ground state as due to a simple spin-up/spin-down situation and the impetus for believing it could be switched to the spin-up/spin-up maximum by changes to a *single* spin alignment. The successful achievement of the latter, and its explanation by DFT, for such a high Mn$_7$ nuclearity argues well for further targeted manipulations of S values at even higher nuclearities. We emphasize that the small absolute magnitude of the calculated $J_{22(i)}$ and $J_{23(i)}$ interactions and their expected uncertainties means that it would have been unreliable to have used the DFT results by themselves to predict the ground-state S values of **1** and **2**. Instead, we are merely using the DFT results to rationalize the experimentally established results, and this has led to the conclusion that the ground state and its switching are ultimately determined by the relative magnitude of these two weakest interactions. We are now exploring the use of pressure to fine-tune the switch in the ground state from $S = 11$ to $S = 16$.

Supporting Information Available: Crystallographic data (CIF format) for **1** and **2**, magnetism figures, and DFT tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) A previous attempt to probe the origin of the $S = 11$ ground state in this Mn$_7$ family assumed that all interactions between the outer and inner Mn atoms were identical, i.e., $J_{22(i)} = J_{23(i)}$.[4c] We did not feel that this approximation was a safe one, and this is borne out by the present work, which reveals the $J_{22(i)}$ and $J_{23(i)}$ difference to be crucial to the observed ground state.

(10) Full details of the magnetic studies and structural comparisons of **1**, **2**, and others will be provided in a full paper.